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(54) **Method of forming molybdenum carbide catalyst**

(57) A molybdenum carbide compound is formed by reacting a molybdate with a mixture of hydrogen and carbon monoxide. By heating the molybdate powder from a temperature below 300 °C to maximum temperature 850 °C, a controlled reaction can be conducted wherein molybdenum carbide is formed. A high surface area, nanograin, metastable molybdenum carbide can be formed when the reaction temperature is below 750 °C. The metastable molybdenum carbide is particularly suitable for use as a catalyst for the methane dry reforming reaction.

**EP 1 088 788 A2**

## Description

[0001] Synthesis gas is a mixture of hydrogen and carbon monoxide, which is formed from methane reforming and has a variety of different applications in organic reactions. This can be formed by combining steam and oxygen with methane at high temperatures. Another method of forming synthesis gas from methane is the methane dry reforming reaction. In this reaction, carbon dioxide is mixed with methane and the blend is subjected to high temperature in the presence of a catalyst. This in turn forms hydrogen and carbon monoxide. The hydrogen from the reforming process is particularly suitable for use in fuel cell power systems.

[0002] The typical catalyst for use in the methane dry reforming reaction is a noble metal such as gold, platinum or the like. However, these catalysts tend to be relatively expensive. Molybdenum carbide is known as a catalyst for such reaction. However, this can be difficult to form. Further for use as a catalyst, high surface area is critical. Molybdenum carbide tends to form larger grains having reduced surface areas which in turn reduces its effectiveness as a catalyst. Thus, because of this problem and the high temperature and time required to form molybdenum carbide, it has not been used commercially as a catalyst for the methane dry reforming reaction.

[0003] The present invention is premised on the realization that a molybdenum carbide catalyst suitable for use in the methane dry reforming reaction as well as other reactions can be formed at relatively low temperatures and in relatively short periods of time. These reactions also include fuel processing as applicable in fuel cell uses.

[0004] More particularly the present invention is premised on the realization that molybdates such as ammonium molybdate can be directly formed into a high surface area molybdenum carbide by direct reaction with a mixture of hydrogen and carbon monoxide. The molybdate is heated from a temperature below 300 °C to a temperature below 850 °C at a ramp rate of about 2-20 °C/min in the presence of the hydrogen, carbon monoxide mixture. This permits the molybdate to be reduced and then carburized directly to molybdenum carbide.

[0005] The formed molybdenum carbide has a high surface area in the range of 35-100 m<sup>2</sup>/g and has a metastable Mo<sub>2</sub>C structure with very diffused X-ray diffraction peaks. The carbide powder can be used as a catalyst in the methane dry reforming reaction to obtain nearly theoretical yields of hydrogen and carbon monoxide at a temperature of 850 °C.

[0006] According to the present invention, a molybdenum carbide powder is formed from a molybdate by reacting it under 750 °C with a mixture of a reducing and carburizing gases, which are specifically hydrogen and carbon monoxide. The formed carbide has a structure of Mo<sub>2</sub>C<sub>y</sub>, wherein y represents 0.95 to 1.05.

[0007] The starting molybdate can be any molybdate wherein the counter ion is not a metal. Generally, the counter ion will be an organic compound or ammonium which is preferred due to its availability. Other molybdenum compounds such as molybdenum oxides can also be used.

[0008] The reaction gas would be a blend of hydrogen and carbon monoxide at a ratio between 3:1 to 1:1 and preferably at 1:1 ratio (by volume). Other carburizing gases such as methane or ethylene can also be used.

[0009] The reaction can be conducted in any suitable furnace which permits control of the gaseous atmosphere and temperature. A rotary kiln is particularly suitable due to its ability to ensure adequate mixing of the solid and gaseous reactants. The ammonium molybdate powder is simply loaded into a quartz liner and placed into the rotary kiln.

[0010] The system is purged with nitrogen first and then the hydrogen, carbon monoxide mixture is introduced. The temperature can be quickly raised to 300 °C and thereafter the temperature ramp rate should not exceed 20 °C/min and preferably is 2-20 °C/min. The reaction temperature and the furnace temperature ramp rate are critical for practicing the present invention. The molybdate starts decomposition at about 300 °C. It decomposes into oxides, which at some stage can be amorphous. The reduction and carburization of the resulting oxide occurs at the same time when the temperature goes above 400 °C. A 3- to 5-hour soak at a temperature between 550° to 600 °C provides enough time for molybdenum carbide to nucleate and a higher temperature will expedite the formation of molybdenum carbide.

[0011] The maximum temperature should not exceed 850 °C and most preferably be less than 750 °C. At 700 °C, the reaction can be completed in 2 to 4 hours. The reaction time can be shortened by increasing the reaction temperature at the expense of increasing grain size and reducing surface area.

[0012] During the reaction, the feeding gas composition can be changed if desired in order to adjust the total carbon content of the powder. Subsequently, the reactor is cooled down with flowing hydrogen, carbon monoxide mixture, hydrogen alone, or nitrogen. Because of the high surface area, the powder should be passivated with diluted oxygen or air after the powder cools down to room temperature.

[0013] The molybdenum carbide formed in this manner is a metastable Mo<sub>2</sub>C<sub>y</sub>. X-ray diffraction on the carbide powder shows some missing peaks in the diffraction pattern. At this stage, the powder samples exhibit specific surface areas of over 35 m<sup>2</sup>/g. Catalysis tests on the carbide powder for the methane dry reforming reaction indicate that the defect Mo<sub>2</sub>C<sub>y</sub> crystal structure may be responsible for the high catalysis activity of the powder.

[0014] The invention will be further appreciated in

light of the following detailed examples.

#### Example 1

[0015] 450 g of ammonium molybdate powder was loaded in a rotary kiln and heated to 590 °C and then 760 °C at a ramp rate of about 10 °C/min in a gaseous mixture of H<sub>2</sub> and CO at 1:1 volume ratio. The soak time is 5 hours at 590 °C and 3 hours at 760 °C. After the furnace cooled down to room temperature, the powder was passivated with a dilute air for about 1 hour. XRD on the product powder shows Mo<sub>2</sub>C. The BET specific surface area of the powder was 18.5 m<sup>2</sup>/g. Carbon analysis on the powder showed 5.84% combined carbon and 1.72% free carbon.

#### Example 2

[0016] 450 g of ammonium molybdate powder was loaded in a rotary kiln and heated to 590 °C and then 700 °C at a ramp rate of about 10 °C/min in a gaseous mixture of H<sub>2</sub> and CO at 1:1 volume ratio. The soak time is 5 hours at 590 °C and 3 hours at 700 °C. After the furnace cooled down to room temperature, the powder was passivated with a dilute air for about 1 hour. XRD on the product powder shows defect Mo<sub>2</sub>C with some missing peaks in the XRD pattern. The BET specific surface area of the powder was 37.7 m<sup>2</sup>/g. Carbon analysis on the powder showed 6.07% combined carbon and 1.62% free carbon.

#### Example 3

[0017] 450 g of ammonium molybdate powder was loaded in a rotary kiln and heated to 700 °C at a ramp rate of about 10 °C/min in a gaseous mixture of H<sub>2</sub> and CO at 1:1 volume ratio. The soak time is 5 hours at 700 °C. After the furnace cooled down to room temperature, the powder was passivated with a dilute air for about 1 hour. XRD on the product powder shows defect Mo<sub>2</sub>C with some missing peaks in the XRD pattern. The BET specific surface area of the powder was 35.7 m<sup>2</sup>/g. Carbon analysis on the powder showed 5.99% combined carbon and 2.15% free carbon.

#### Example 4

[0018] 720 g of ammonium molybdate powder was loaded in a production tube furnace and heated to 582 °C and then 699 °C at a ramp rate of about 8 °C/min in a gaseous mixture of H<sub>2</sub> and CO at 3:1 volume ratio. The soak time is 10 hours at 582 °C and 3 hours at 699 °C. After 3 hours carburization at 699 °C, additional 16% CO<sub>2</sub> was introduced for free carbon removal. The decarburization was performed for another 3 hours. After the furnace cooled down in N<sub>2</sub> to room temperature, the powder was passivated with a dilute air. XRD on the product powder showed Mo<sub>2</sub>C and a XRD peak

broadening technique gave a Mo<sub>2</sub>C grain size of 26 nm. The BET specific surface area of the powder was 39 m<sup>2</sup>/g. Carbon analysis on the powder showed 5.53% combined carbon and <0.04% free carbon.

#### Example 5

[0019] A methane dry reforming catalyst test was done on the metastable Mo<sub>2</sub>C powder synthesized as shown in example 2. The test was performed in a small tube furnace. Two quartz wool plugs were used to keep 5 g Mo<sub>2</sub>C powder layer in between and permit the reacting gases passing through. Mass flow meters were used to control the gas flow and a 3-channel (CH<sub>4</sub>/CO/CO<sub>2</sub>) IR analyzer was used to monitor the inlet and outlet gas compositions. The test showed 47% CO yield initially, which is very close to the equilibrium 49% CO yield. This high CO yield was kept for over 48 hours. Then, the yield dropped to and stabilized at about 25% for another 24 hours. The test was interrupted after 72 hours. Catalytic activity was still obvious, even after 72 hours of reaction.

[0020] This has been a description of the present invention along with the preferred method of practicing the present invention.

#### Claims

1. A method of forming a Mo<sub>2</sub>C<sub>y</sub> compound wherein y is 0.95 to 1.05 comprising heating a molybdenum compound from a temperature of less than 300 °C to less than 850 °C at a ramp rate of 2 to 20 °C/min in a gaseous blend of a reducing gas and a carburizing gas for a time effective to convert said molybdenum compound to Mo<sub>2</sub>C<sub>y</sub>.
2. The method claimed in claim 1 wherein said gaseous blend is selected from the group consisting of a mixture of hydrogen and carbon monoxide, and a mixture of hydrogen, carbon monoxide and carbon dioxide.
3. The method claimed in claim 1 wherein said gaseous blend is a mixture of hydrogen and carbon monoxide having a volume ratio of 3:1 to 1:1.
4. The method claimed in claim 1 wherein said molybdenum compound is heated to a temperature from 300 °C to 750 °C.
5. The method claimed in claim 1 wherein said molybdenum compound is a molybdate.
6. The method claimed in claim 1 wherein said carburizing gas is selected from the group consisting of carbon monoxide, carbon dioxide, methane, ethylene and mixtures thereof.

7. The method claimed in claim 1 further comprising passivating said formed  $\text{Mo}_2\text{C}_\gamma$  with diluted oxygen.
8. The method claimed in claim 1 comprising soaking said molybdenum compound at a temperature of 550 to 600 °C for 2 to 5 hours.
9. A metastate  $\text{Mo}_2\text{C}_\gamma$  wherein  $\gamma$  is 0.95 to 1.05 having a specific surface area greater than about 35 m<sup>2</sup> /g.
10. The product made by the process claimed in claim 1.
11. The product made by the process claimed in claim 2.
12. The product made by the process claimed in claim 3.
13. The product made by the process claimed in claim 4.
14. The product made by the process claimed in claim 5.
15. The product made by the process claimed in claim 6.
16. The product made by the process claimed in claim 7.
17. The product made by the process claimed in claim 8.
18. A method of forming hydrogen from a mixture of methane and carbon dioxide comprising contacting said mixture with the catalyst formed by the method claimed in claim 1 for a time and at a temperature effective to cause said methane and carbon dioxide to react to form hydrogen and carbon monoxide.

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## EUROPEAN SEARCH REPORT

Application Number  
EP 00 20 3035

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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X	ATTILA J. BRUNGS ET AL.: "Comparison of the group V and VI transition metal carbides for methane dry reforming and thermodynamic prediction of their relative stabilities" CATALYSIS LETTERS., vol. 57, no. 1, 2, February 1999 (1999-02), pages 65-69, XP002159539 BALTZER, SCIENTIFIC PUBL, BASEL., CH ISSN: 1011-372X * the whole document *	9	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C01B B01J
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 6 February 2001	Examiner Rigondaud, B
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

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Place of search THE HAGUE		Date of completion of the search 6 February 2001	Examiner Rigondaud, B
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DOCUMENTS CONSIDERED TO BE RELEVANT			
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A	<p>EPICIER T ET AL: "Neutron powder diffraction studies of transition metal hemicarbides <math>M_2C_{1-x}</math> - II. In situ high temperature study on <math>W_2C_{1-x}</math> and <math>Mo_2C_{1-x}</math>"</p> <p>ACTA METALL AUG 1988, vol. 36, no. 8, August 1988 (1988-08), pages 1903-1921, XP000981573</p> <p>* the whole document *</p>	9	
			TECHNICAL FIELDS SEARCHED (Incl.7)
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		6 February 2001	Rigondaud, B
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document</p>			

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**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

100